

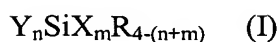
PATENT CLAIMS

1. Composition which cures using visible light containing

- (a) 2-99 wt.% of at least one compound which contains at least one acrylate group and/or at least one methacrylate group and/or at least one vinyl group and/or at least one epoxy group and/or at least one oxetane group and/or at least one acryl-epoxy oligomer group and/or at least one methacryl-epoxy oligomer group, and/or at least one resin composition based on at least one polymerisable polysiloxane,
- (b) 0.01-7 wt.% of at least one initiator,
- (c) 0-5 wt.% of at least one co-initiator,
- (d) 0-85 wt.% of one or more modifiers, such as fillers, dyestuffs, pigments, flow improvers, thixotropic agents, polymeric thickeners, oxidising additives, stabilisers and retardants.

2. Composition according to claim 1, characterised in that at least one ormocer is present in the resin composition as polymerisable polysiloxane.

3. Composition according to claim 1 or 2, characterised in that as resin composition, a resin composition based on polymerisable polysiloxanes which can be hardened photochemically or thermally in the presence of initiators or one which is self-hardening, which can be obtained by hydrolytic condensation of one or more hydrolytically condensable compounds of silicon and optionally other elements from the group B, Ba, Ti, Zr, Al, Sn, the transition metals, the lanthanides and the actinides, and/or pre-condensates derived from the above-mentioned compounds, optionally in the presence of a catalyst and/or a solvent, by the action of water or moisture, wherein 1 to 100 mole %, based on the monomeric compounds, are selected from silanes of the general formula (I),



in which the radicals X, Y and R are the same or different and have the following meaning:

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl

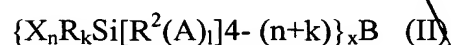
X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl, or NR'_2 where

R' = hydrogen, alkyl or aryl,

Y = a substituent, which contains a substituted or unsubstituted 1,4,6-trioxyaspiro-[4,4]-nonane radical,

n = 1, 2 or 3, m = 1, 2 or 3, where $n+m \leq 4$,

and/or from silanes of the general formula (II),



in which the radicals A, R, R_2 and x are the same or different and have the following meaning:

A = O, S, PR', POR', $\text{NHC}(\text{O})\text{O}$ or $\text{NHC}(\text{O})\text{NR}'$, where R' = hydrogen, alkyl or aryl,

B = straight-chain or branched organic radical, which is derived from a compound B' having at least one (for $l = 1$ and $A = \text{NHC}(\text{O})\text{O}$ or $\text{NHC}(\text{O})\text{NR}'$) or at least two $\text{C}=\text{C}$ double bonds and 5 to 50 carbon atoms, where R' = hydrogen, alkyl or aryl,

R = alkyl, alkenyl, aryl, alkylaryl or arylalkyl,

R^2 = alkylene, arylene or alkylene-arylene,

X = hydrogen, halogen, hydroxyl, alkoxy, acyloxy, alkylcarbonyl, alkoxycarbonyl or NR'_2 , where

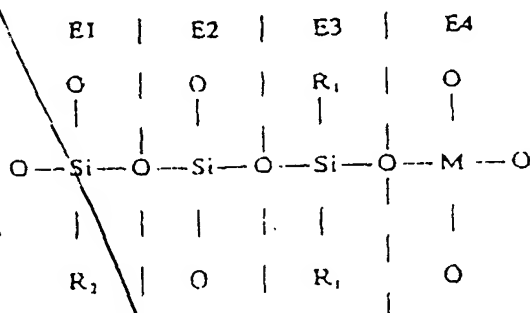
R' = hydrogen, alkyl or aryl,

n = 1, 2, or 3, k = 0, 1 or 2, l = 0 or 1,

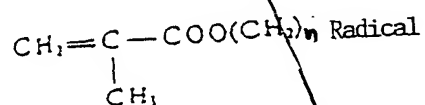
x = a whole number, the maximum value of which corresponds to the number of double bonds in the compound B' minus 1, or is equal to the number of double bonds in the compound B', when $l = 1$ and A represents $\text{NHC}(\text{O})$ or $\text{NHC}(\text{O})\text{NR}'$,

optionally containing fillers and/or copolymerisable monomers.

4. Composition according to one of claims 1 to 3, characterised in that a compound composed of the structural element E 2 and at least one of the structural elements E 1 and/or E 3 and/or E 4 of the general formula



wherein R₁ denotes a methyl, ethyl, n-propyl, isopropyl or an optionally CH₃-C₃H₇-substituted phenyl radical, R₂ denotes a CH₂=CH, CH₂=CHCOO(CH₂)_n or



or R₁, n denotes 0, 1, 2 or 3, and M denotes titanium or zirconium, is present in the resin composition.

5. Composition according to one of claims 1 to 4, characterised in that it contains the compound of constituent (a) in a quantity of 10-95 wt. %.

6. Composition according to one of claims 1 to 5, characterised in that the composition can be cured in a wavelength range from 350-700 nm.

7. Composition according to one of claims 1 to 6, characterised in that constituent (a) contains aliphatic diurethane methacrylate, tetra-ethoxylated bisphenol A dimethacrylate, aliphatic urethane methacrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, iso-propyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, methacrylic acid esters, isobornyl methacrylate, benzyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, ethyl triglycol methacrylate, tetrahydrofurfuryl methacrylate, hydroxyalkyl methacrylates, 2-hydroxyethyl methacrylate, alkoxyethyl methacrylate, allyl methacrylate, ethylene glycol dimethacrylate, diethyl glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylates, 1,3-butane diol dimethacrylate, 1,4-butane diol dimethacrylate, 1,6-hexane diol dimethacrylate, 1,12-dodecane diol dimethacrylate, glycerin-1,3-dimethacrylate, diurethane dimethacrylate, trimethylol propane trimethylacrylate, 1,3,5,7-tetrakis-(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7-tetramethylcyclotetrasiloxane, 1,10-decanediyl-bis(oxymethylene)bis(3-ethyloxetane), 1,3,5,7,9-pentakis(2,1-ethanediyl-3,4-epoxycyclohexyl)-1,3,5,7,9-pentamethylcyclopentasiloxane, vinylcyclohexene oxide, vinylcyclohexene dioxide, 3,4-epoxy-6-methylcyclohexylmethyl-3,4-epoxy-6-methylcyclohexane carboxylate, bis(2,3-epoxycyclopentyl)ether; 3,4-epoxy-6-methylcyclohexylmethyl adipate, 3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy(cyclohexane-metadioxane), 1,4-butanediyl-bis(oxymethylene)bis(3-ethyloxetane), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 1,1,3,3-tetramethyl-1,3-bis(2,1-ethanediyl-3,4-epoxycyclohexyl)disiloxane, bis-(3,4-epoxycyclohexylmethyl) adipate, monovinyl ether, divinyl ether, hydroxyvinyl ether, aminovinyl ether, trivinyl

ether, triethylene glycol divinyl ether, 4-hydroxybutylvinyl ether, propenyl ether from propylene carbonate, dodecyl-vinyl ether, triethylene glycol divinyl ether, alkyl-vinyl ether, ethylene glycol-monovinyl ether, diethylene glycol divinyl ether, butane diol-monovinyl ether, butane diol-divinyl ether, hexane diol-divinyl ether, ethylene glycol-butyl-vinyl ether, cyclohexane-dimethanol-monovinyl ether and cyclohexane-dimethanol-divinyl ether, 2-ethyl-hexyl-vinyl ether, poly-THF-divinyl ether, cyclohexyl-vinyl ether, tert.-butyl-vinyl ether, tert.-amyl-vinyl ether, ethylene glycol-divinyl ether, diethylene glycol-monovinyl ether, hexane diol-monovinyl ether, tetraethylene glycol-divinyl ether, trimethylol-propane-trivinyl ether, aminopropylvinyl ether and/or 2-diethylaminoethyl-vinyl ether.

8. Composition according to one of claims 1 to 7, characterised in that constituent (b) contains for free-radical hardening, phosphine oxides, benzoin ethers, benzil ketals, acetophenones, benzophenones, thioxan^Athones, α -dicarbonyl compounds, bisimidazoles, metallocenes, aryl-tert.-butyl peresters and/or fluorones, for cationic hardening, aryl diazonium salts, aryl sulphonium salts, aryl iodonium salts, ferrocenium salts and/or phenylphosphonium-benzophenone salts or a mixture thereof.

9. Composition according to claim 8, characterised in that as phosphine oxide, diphenyl-2,4,6-trimethylbenzoylphosphine oxide, as benzoin ether, benzoin and/or benzoin-alkyl ether, as benzil ketals, benzil dialkyl ketals, as acetophenones, α -hydroxyacetophenones, dialkoxyacetophenones and/or α -aminoacetophenones, as thioxanthone, i-propylthioxanthone, as α -dicarbonyl compound, camphor-quinone, as metallocenes, titanocenes and/or ferrocenes, as fluorones, 5,7-diiodo-3-butoxy-6-fluorones, are present.

10. Composition according to one of claims 1 to 9, characterised in that constituent (c) contains for free-radical hardening, tertiary amines, diaryl iodonium compounds, borates, organic phosphites and/or thioxan^Athones,

for cationic hardening, xanthenes, fluorenes, fluorones and/or α -dicarbonyl compound, or a mixture thereof.

11. Composition according to claim 10, characterised in that as tertiary amine, N,N-dimethyl-p-toluidine, N,N-dihydroxyethyl-p-toluidine, N,N-dialkyl-alkylaniline and/or other structure-related amines, as borates, butyrylcholine-triphenylbutyl borate and/or other structure-related borates, are present.

12. Composition according to one of claims 1 to 11, characterised in that constituent (d) contains an anthraquinone dyestuff.

13. Composition according to one of claims 1 to 12, characterised in that constituent (d) contains as filler, silicon dioxide, pyrogenic silicon dioxide, amorphous silicic acid, aluminium oxide, ceramic, quartz, ground glass, fragment polymer, silica gel, minerals, fibres and/or fabrics.

14. Composition according to claim 13, characterised in that as fibres and/or fabrics, glass fibres, carbon fibres, textile fibres and/or metal fibres, are present individually or in tape, mat, hose or cord form or in the form of a bundle of continuous fibres.

15. Composition according to claim 14, characterised in that one or more of the fillers present are silanised.

16. Composition according to one of claims 1 to 15, characterised in that constituent (d) contains hydroquinone, hydroquinone monomethyl ether, pyrocatechol, 2,6-di-tert.-butyl-4-methylphenol.

17. Use of a composition according to one of claims 1 to 16 in a shaping process.

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18. Use of a composition according to one of claims 1 to 16 for producing models, individually manufactured single products and mass-produced sales products.

19. Use of a composition according to one of claims 1 to 16 in a process of microsolidification, rapid-prototyping, film casting, the production of plastic sintered parts, microstructuring, photolithography, the production of dental products, the production of surgical implants and/or the production of otoplastic products.

20. Use of a composition according to one of claims 1 to 16 in a process for producing a three-dimensional object by sequential selective solidification of layers of the composition at positions corresponding to the cross-section of the object under the action of visible light.

21. Process for producing a tooth filling by sequential layered solidification of a composition according to one of claims 1 to 13 at positions corresponding to the cross-section of the filling in the particular layer.

22. Process according to claim 21, characterised by the steps

- a) producing a computer model of the filling to be produced,
- b) dividing the computer model into layers, which correspond in each case to a cross-section of the filling,
- c) layered curing of the composition at positions corresponding to the cross-section of the filling under the action of visible light.

23. Process according to claim 21 or 22, characterised in that a paste-like composition is used.

24. Process according to claim 23, characterised in that glass-fibre constituents are admixed to the composition.

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25. Object which is produced by curing the composition according to one of claims 1 to 13 by means of visible light.

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